APPLICATIONS OF THE GV INSTRUMENTS TRACE GAS FOR METHANE AND CARBON DIOXIDE ISOTOPE STUDIES: LONDON DIURNALS AND IRISH WETLAND EMISSIONS

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ABSTRACT

Small-scale modifications to a continuous flow GC-IRMS system, the GV Instruments Trace Gas and IsoPrime, have enabled isotopic analysis of methane and carbon dioxide to be made in 75 cm^3 of ambient air with a reproducibility of 0.05‰ for δ^{13}C in CH_4, 0.03‰ for δ^{13}C in CO_2 and 0.05‰ for δ^{18}O in CO_2 (1σ, n=10).

An automated inlet has been installed to allow the Trace Gas to run continuously, measuring air either directly from an intake on the roof or from tanks connected to the inlet. The system allows frequent diurnal studies to be carried out at Royal Holloway which is situated 32km west of the centre of London. Isotope measurements are made at 30 minute intervals, at the same time as concentration measurements are made on a HP 5890 gas chromatograph and LICOR CO_2 analyser in the laboratory. The method provides a fast turn around in samples with accurate, reproducible results and would allow a long-term continuous record of CH_4 or CO_2 isotopes to be made, providing information about changing sources of the gases in the London region, both seasonally and inter-annually. The Royal Holloway sampling site is ideally situated to measure near background air from the south-west or London air from the east. During high pressure anticyclonic events coinciding with a low wind speed there can be a large build-up in concentrations of methane and carbon dioxide as an inversion builds up over the London basin. Measurements at high frequency intervals allow individual source plumes to be identified and comparison with wind direction measurements can lead to identification of local sources. Source calculations from preliminary diurnal studies show that local sources have δ^{13}C values of between -34‰ (typical of gas leaks) and -54‰ (likely to be landfill sites). Carbon dioxide diurnal studies indicate an average CO_2 δ^{13}C source for air coming from the East, i.e. from the direction of London of -30.4‰.

Source studies were carried out in wetlands in Ireland during three sampling campaigns in 2004 and 2005. Samples of ambient air were collected upwind and downwind of wetlands (blanket bogs, raised bogs and fens) and analysed using the Trace Gas and the isotopic composition of the source calculated. Small, but measurable differences in the concentrations and isotope values upwind and downwind of the sites were compared with isotope measurements of methane and carbon dioxide accumulated in closed chambers at each of the sites. Highest emission rates and most depleted methane (values down to -81‰) occurred at raised bogs which are primarily located in the midlands of Ireland. The raised bogs were also found to be a CO_2 source with δ$^{13}C_{CO2}$ values of the order of -21‰. Although on a global scale Irish wetland emissions of methane are relatively small: approximately 0.4 Tg/yr compared to the global wetland emission estimate of ~160 Tg/yr, they are comparable to the size of Ireland's anthropogenic methane emissions (~0.6 Tg/yr).

The small sample volumes and rapid analysis time provided by continuous flow instrumentation such as the Trace Gas has rapidly increased the number and type of samples that can be analysed. The improvements mean that it is approaching the precision required to monitor seasonal shifts in $^{13}CH_4$ at background sites, with automation of the instrumentation allowing continuous monitoring of the isotopic composition of CH_4 or CO_2 at a fixed site.

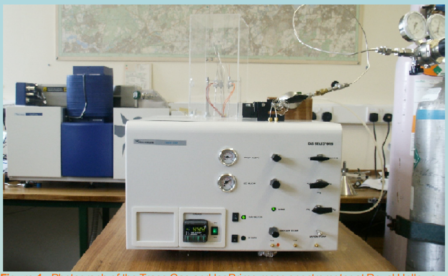

Figure 1. Photograph of the Trace Gas and IsoPrime mass spectrometer at Royal Holloway. The instruments were installed in February 2003. Whitey valves on the front panel of the Trace Gas are used to select the gas to be analysed: CH_4, CO_2 or N_2O. The system uses small volume samples, 75 cm^3, and each analysis takes 16 minutes. Since installation small modifications have been made to the system, to improve the precision achieved in methane δ^{13}C analysis. Use of a palladised quartz wool catalyst improved the efficiency of combustion of methane to carbon dioxide and a fixed automated inlet system removed variations in timings and contamination with laboratory air. Since this development work precisions of 0.05‰ for δ^{13}C in methane, 0.03‰ for δ^{13}C in CO_2 and 0.05‰ for δ^{18}O in CO_2 have been achieved in 10 analyses of a secondary standard tank.

DIURNAL STUDIES IN THE LONDON REGION

Continuous methane (30 minute interval) and carbon dioxide (5 minute interval) mixing ratio monitoring has been carried out at Royal Holloway (RHUL) since 1995 for CH_4 and 1999 for CO_2 (fig. 2). The RHUL site (fig. 3) is well situated to measure fairly clean, near background air from the South-West (the prevailing wind direction) and polluted air from London and the continent to the East. Under anticyclonic conditions coinciding with a low wind speed an inversion often builds up in the London basin and CH_4 and CO_2 mixing ratios are particularly high.

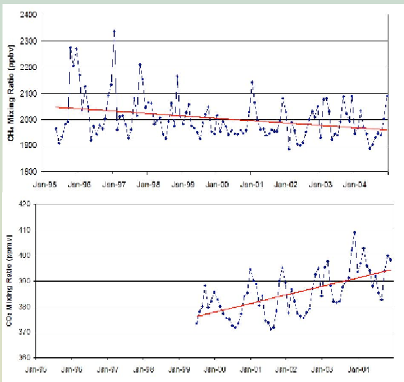

Figure 2. Methane (top graph) and carbon dioxide mixing ratio measured at Royal Holloway. Methane mixing ratio has decreased over the last decade by ~9 ppbv yr^{-1} on average. There have been fewer strongly polluting events in recent years. This may in part be due to meteorology, but there is also evidence for a decrease in the magnitude of some methane sources. Maximum methane concentrations occur between December and February. Carbon dioxide mixing ratios have been increasing by ~3 ppmv yr^{-1}. Continuing isotope measurements over a period of time may provide information about changing source strengths and help understand changes in the mixing ratio record.

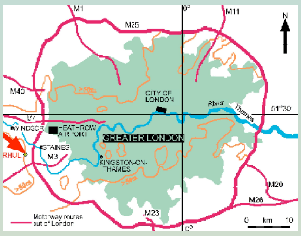

Figure 3. Location of the RHUL sampling site. RHUL is situated 32 km from the centre of London, on the first significant incline WSW of the city. The air inlet is on the roof of the Geology department, 15m above ground level.

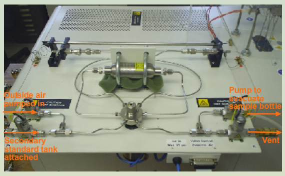

Figure 4. The automated inlet system on the Trace Gas. The sample bottle volume is 75 cm^3. While the bottle is filled the Trace Gas connections are purged with helium and when the bottle is full the 6-port valve is switched to direct the air sample into the Trace Gas. One 2-way valve is attached to a pump connected to an inlet on the roof of the building. Outside air vents through as the bottle is filled. Alternatively the sample bottle is evacuated and filled with air from a secondary standard tank which is permanently connected and analysed regularly to check stability of the system.

Addition of an automated inlet sytem (fig. 4) in November 2004 means that the Trace Gas can be run semi-continuously, analysing the isotopic composition of either methane or carbon dioxide in outside air at half hourly intervals. At present the system is run overnight when meteorological conditions are such that a large build up in mixing ratio is likely to occur.

(i) CO2 Diurnal Studies

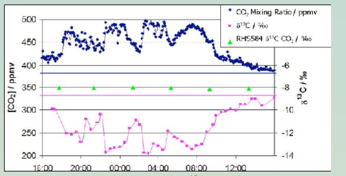

Figure 5. CO_2 Mixing ratio (blue) and δ^{13}C CO_2 (pink) during a 24 hour period, February 7th-8th 2005. The horizontal pink and blue lines denote background levels. Secondary standard tank analyses are also shown (green) and illustrate the reproducibility achieved (standard deviation = 0.03‰).

Analysis at 30-minute intervals allows individual source plumes to be measured as the wind changes direction (fig. 5). Results can be subdivided according to wind direction and Keeling plots are used to estimate the source signature of excess CO_2 over background from different sectors. The easterly sector, i.e. the direction of London, has a source signature of -30.4‰ (fig. 6). The source signature varies according to time of day (fig. 7). Overnight minima at -33‰ are dominated by fossil fuel combustion, wheras during the day the source is more enriched at -17‰ due to photosynthesis.

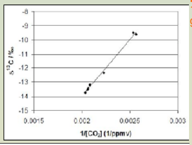

Figure 6. Keeling plot for wind from the East during the diurnal February 7th-8th 2005. The intercept of the line at -30.4‰ denotes the source signature for London.

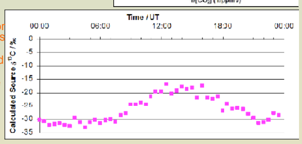

Figure 7. Source calculations for all CO_2 diurnals carried out to date averaged over time to show how the source signature changes with time of day.

(ii) CH4 Diurnal Studies

Results from CH_4 diuranls at RHUL are strongly affected by wind direction. For example during the diurnal shown in fig. 8 the wind direction was primarily from the West. Results show an enrichment in δ^{13}C as mixing ratios increase, caused by enriched CH_4 sources, such as gas leaks at -34‰. During the diurnal shown in fig. 9 the wind direction was from the East. The methane source in this direction caused a depletion in δ^{13}C as mixing ratio increased, as a result of biogenic emissions, mainly landfill at -54‰. Carrying out diurnals throughout the year will provide information on the annual variability in methane sources. Initial results (fig. 10) indicate that the source signature in the winter is significantly enriched compared with in the summer, as would be expected from gas boilers being turned on and lower landfill emissions at low temperatures. However only two diurnal studies have been carried out in the winter so far so results are biased towards particular wind directions.

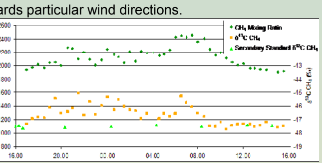

Figure 8. CH_4 mixing ratio (dark green) and δ^{13}C CH_4 (orange), March 9th-10th 2005. WInd direction W-WNW. Secondary standard tank analyses (light green) have a standard deviation of 0.05‰.

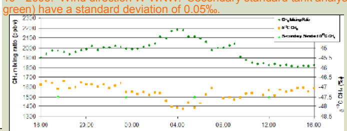

Figure 9. CH_4 mixing ratio (dark green) and δ^{13}C CH_4 (orange), July 27th-28th 2005. Wind direction E.

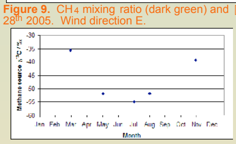

Figure 10. Source signature of excess methane over background for diurnals carried out in March (1 diurnal), May (3), July (3), August (9) and November (1).

IRISH WETLAND STUDIES

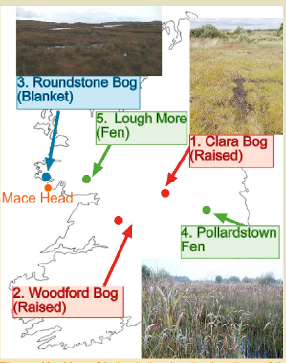

Figure 11. Map of Ireland showing the locations of the sampling areas and photos of Roundstone bog, Clara bog and Pollardstown fen.

Three sampling campaigns, in June and October 2004 and June 2005 have been carried out to measure the isotopic composition of CH_4 and CO_2 emitted by wetlands in Ireland. Peatlands cover an area of 1 177 000 ha in Ireland, although >80% has been affected by drainage and peat cutting. Sample locations are shown in fig. 11 and include raised bog (mainly found in the midlands), Atlantic blanket bog (found along the west coast) and fens.

Air was collected in chambers and measured upwind and downwind of the wetland areas and the CH_4 and CO_2 mixing ratios and isotopic compositions measured. Table 1 summarises the results of methane studies from the October 2004 and June 2005 sampling campaigns. There was significant spatial variability in the emission rates and isotopic composition within each bog which limits the reliability in estimations of the overall source signature. Therefore comparison between the upwind and downwind isotopic compositions may give more realistic values for the whole wetland area. However the isotopic difference between measurements either side of the wetland is not always measurable, particularly if the wind speed is high or wind direction is inconsistent.

Type	Site	Mean Emission rate	Mean δ^{13}C (October '04)	Mean δ^{13}C (June '05)	Upwind/Downwind Source Signature (June '05)
Raised	Clara	0.17 μgs^{-1}m^{-2}	-81.1‰	-76.4‰	-77.63‰
Raised	Woodford	0.10 μgs^{-1}m^{-2}	-78.6‰	-78.9‰	
Blanket	Roundstone	0.13 μgs^{-1}m^{-2}	-73.7‰	-81.8‰	-56.97‰
Fen	Pollardstown	0.63 μgs^{-1}m^{-2}	-65.9‰	-68.3‰	-66.81‰
Fen	Lough More	0.17 μgs^{-1}m^{-2}	-64.5‰	-74.1‰	-57.14‰

Table 1. Some results from the October sampling campaign. Emission rates are calculated from the build up in methane concentration in a closed chamber over time. The source signature of the methane emitted is calculated from the δ^{13}C as methane builds up in the chamber and from a comparison of upwind and downwind methane mixing ratios and corresponding δ^{13}C.

Figure 12. 15L closed chamber set up at Clara bog. The photo illustrates the inhomogeneity of the wetlands.

Taking into account average emission rates, and the relative area of each wetland type in Ireland,an estimated source signature for methane from Irish wetlands was found to be -70‰, with a total emission rate of 0.4 Tg yr^{-1}. This is small by global standards but is comparable to the size of anthropogenic CH_4 emissions from Ireland, 0.6 Tg yr^{-1}.

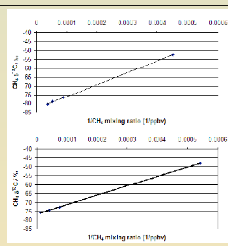

Figure 13. Keeling plots for chambers at Clara bog in October 2004 (top) and June 2005 (bottom). The y-axis intercept of the plots indicates the source signature of emitted CH_4: -81‰ in October and -76‰ in June.

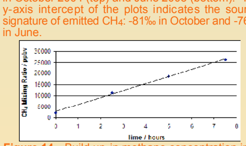

Figure 14. Build up in methane concentration in a closed chamber against time at Clara bog (October 2004). This technique is used to estimate the emission rate.

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